

INTERSTELLAR MOLECULES

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The American astronomer Hartman in 1904 obtained the first indication that the space between stars is not empty, when he found two absorption lines of singly ionized calcium in the spectrum of the spectroscopic double star δ Orionis. In contrast to the other lines in the stellar spectrum, they showed no periodic variations in wavelength due to the orbital motions of the two stars around each other. The "resting" calcium lines also differed distinctly in appearance from the stellar lines, because they were unusually narrow. Hartman stated exactly the correct significance for his discovery: the resting lines originate in a dilute gas which is between the star and the observer.

In the intervening time, many other absorption lines of interstellar origin have been found. They all arise from neutral or singly ionized atoms, and are from transitions starting at the ground state of the atoms or ions. (Thus, they are so-called resonance lines.) This finding proves the low temperature and the low excitation of the interstellar gas. Only at the end of the 1930's were some absorption lines discovered which could be assigned to simple diatomic molecules. With improved detectors, radio astronomy has made it possible to discover a surprisingly large number of other molecules in the last five years. These consist of up to seven atoms. At present, about 25 molecular species are known, but new

* Numbers in the margin indicate pagination in the original foreign text.

discoveries are being announced steadily. Investigation of the interstellar molecules proves to be an outstanding way to obtain new and better information about the conditions in interstellar space and about the origin of stars.

The Discovery of the Interstellar Molecules

1. Molecular Spectra in General

The spectra of the molecules are far more variable in form than those of the atoms. As is well known, these consist of single lines which correspond to transitions between definite energy states of the atoms. While the energy of an atom depends solely on the arrangement of the electrons, for a molecule there is also the energy of the mutual vibrations of the atoms and of the rotation of the whole molecule. Depending on which portion of the energy is changed, we speak of electronic, vibrational, or rotational transitions, spectra, lines, etc.

Changes of the rotational state require the least energy. Therefore, lines in the far infrared and microwave region correspond to these transitions. The rotational states also often have a fine structure; that is, they consist of several substates. The causes of this splitting are very manifold and depend on the type of molecule. One example is the interaction between molecular rotation and the orbital motion of the electrons (so-called A -doubling)⁽¹⁾. The effect of the inherent rotational momentum (spin) of the atomic nuclei gives rise to a hyperfine structure, which is superimposed on the fine structure. Fine and hyperfine structure transitions are preferably investigated by radio astronomy, as the corresponding lines are often in the decimeter wave region, so that they are well accessible instrumentally. (For instance, the famous 21 cm line of atomic hydrogen is a hyperfine structure line.)

⁽¹⁾ A is the symbol for the orbital momentum of the electrons in the molecule.

There are many rotational states in every vibrational state. Therefore, a whole group of lines or bands corresponds to each vibrational transition. These rotational-vibrational bands lie in the near infrared. One electronic state consists of many vibrational states, which in turn are divided into many rotational states. Therefore, a band system corresponds to each electronic transition. The electronic bands occur in the visible and ultraviolet portion of the spectrum.

The molecular spectrum is greatly simplified under interstellar conditions. In general, the excitation is so slight that only the ground states are occupied. Then only one line occurs out of the bands, and even for the vibrational and electronic spectra we deal with only single lines.

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2. Limitations in the Investigation of Interstellar Molecules

Most observations today are made from the ground. Accordingly, whether or not an interstellar molecule is discovered depends on whether it has suitable lines in those spectral regions for which the atmosphere is transparent. These "windows" extend from 3,000 Å up to the infrared at some 20 μm and then from the millimeter to the meter waves.

The molecules must also occur with a certain frequency in order to be discovered. This lower limit depends on the sensitivity of the detector, and it can certainly be reduced still more. Nevertheless, we will find only compounds of the most common elements, that is, those of hydrogen, carbon, oxygen, nitrogen. The abundance of the molecules, of course, depends not only on the abundance of the atoms making them up but also on the probability of their formation and destruction; i. e., on the physical conditions. Thus, simply constructed and resistant molecules will be most widespread.

If we wish to see the molecular lines in absorption, then there must be a luminous star or a strong radio source, the radiation from which the molecules can absorb, behind the interstellar clouds in which the molecules occur. Because of the general interstellar extinction, space is accessible to us only up to some 3,000 light years distance in the visible and ultraviolet portion of the spectrum. Conditions are far more favorable in the radio region, as the interstellar extinction plays no part here. Furthermore, the excitation conditions are often sufficient to cause the molecules to radiate.

3. Molecule Discoveries in the Visible and Ultraviolet Region of the Spectrum

In 1937, Dunham and Adams discovered a series of unquestionable interstellar lines which they could not assign to any atom or ion. In the following years, it was possible to assign them to the molecules CH, CH⁺ and CN. The lines were found in a large number of stars distributed over the entire sky. Thus, the molecules are widely distributed in interstellar space. As the molecular and atomic lines show the same radial velocity, to the extent that they appear in the same star spectrum, the molecules and atoms occur together.

With one exception, the absorbing molecules are in the ground state. Part of the CN stays in the first excited rotational state, which is $4.7 \cdot 10^{-4}$ eV above the ground state. The ratio of the population numbers follows from the ratio of the strengths of the corresponding absorption lines. According to this, the CN molecules have a temperature of 2.3 K. The significance of this finding first became understandable after the discovery of the so-called 3 K radiation by Penzias and Wilson in 1965. The radiation fills the entire universe homogeneously, and is considered a remnant from a very early

stage in development of the universe. Its spectral energy distribution follows Planck's radiation law for a temperature of 2.7 K. Apparently the CN molecules are "warmed" by this primordial radiation until they come to the same temperature. In the meantime, development of rocket technology has made the ultraviolet portion of the spectrum accessible. H_2 and CO were determined in this way. As hydrogen is the most abundant element in the universe, great attention has been devoted to its molecule for a long time, and theoretical deliberations have been made on its distribution. In 1970, Carruthers found the Lyman band of this molecule at 1100 Å in the spectrum of ϵ Persei, but not in that of ζ Persei. Now the former star is considerably paler than the latter, so that a relation is indicated between paleness and the presence of H_2 . This corresponds to the expectation, because interstellar dust plays a large role in the formation of this and other molecules.

Likewise, Smith and Stecher found absorption in the ultraviolet from CO for ζ Ophiuchi. The density of carbon monoxide is considerably higher than that of CN or CH. This finding can no doubt be explained by the greater stability of CO.

4. Molecular Lines in the Radio Wave Region

Schklowski (1956) first took into consideration the possibility of observing interstellar molecules in the radio wave region. Seven years later, Weinreb, Barrett, Meeks and Henry found absorption lines at the 18 cm wavelength in the spectrum of the strong radio sources Cassiopeia A and Sagittarius A (at the center of the Milky Way) which they ascribed to the hydroxyl radical (OH). The same molecule was also observed in emissions shortly thereafter in the vicinity of a bright diffuse cloud. In 1968, emission lines at a wavelength of 1.3 cm were discovered. They arose from ammonia (NH_3).

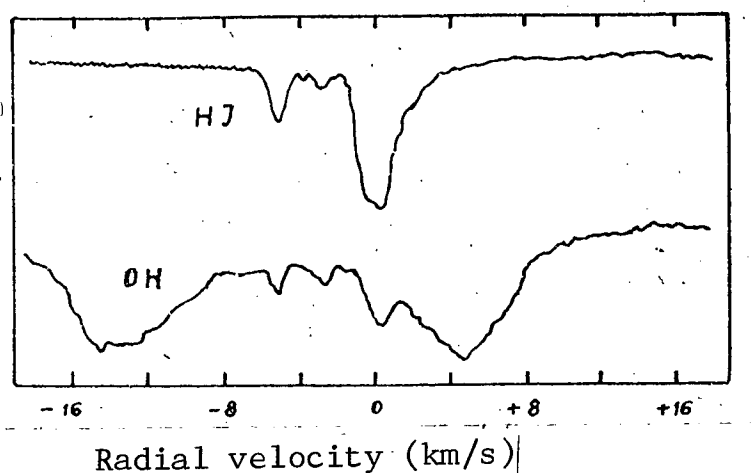


Figure 1: One of the first observations of the hydroxyl radical in absorption in the spectrum of the radio source Sagittarius A (center of the Milky Way). Comparison with the absorption profile of hydrogen shows that the clouds with the greatest OH absorption leave no traces in the 21 cm profile. Perhaps the hydrogen there is predominantly in the molecular form.

That was a great surprise, because it was generally considered that only diatomic molecules occurred. Since then, new molecules have been observed in rapid sequence. These include many diatomic molecules, but most of them are multi-atomic.

The molecules which have become known up to June, 1972 are tabulated in Table 1 in the order of their discovery. Isotopic molecules are not considered. The wavelength data are only approximate. Not all the wavelengths are given at which molecules are observed, but generally only those at which they were discovered. An E and A are used to indicate whether the molecules are observed in emission or in absorption.

The assignment is not reliable in two cases, in which the molecule names are in parentheses. The designation "Xogen" is also common in the previous case.

TABLE 1. LIST OF THE KNOWN INTERSTELLAR MOLECULES

Year	Name	Symbol	Wavelength	Spectrum	Discoverer
1937	Methinyl	CH	4300 Å	A	Dunham/ Swings and Rosenfeld
1940	Cyanogen	CN	3875 Å	A	Adams/ McKellar
1941		CH+	3745-4233 Å	A	Adams/Douglas & Herzberg
1963	Hydroxyl	OH	18, 6.3, 5.0, 2.2 cm	A,E	Weinreb, Barrett, Meeks, Henry
1968	Ammonia	NH ₃	1.3 cm	E	Cheung, Rank, Townes, Thornton & Welch
1969	Water	H ₂ O	1.4 cm	E	Cheung, Rank, Townes, Thornton & Welch
1969	Formaldehyde	HCHO	6.2, 2.1 cm, 2.1, 2.0 mm	E,A	Evans, Cheung & Sloanaker
1970	Carbon monoxide	CO	2.6 mm	E	Wilson, Jefferts & Penzias
1970	Cyanogen	CN	2.6 mm	E	Jefferts, Penzias & Wilson
1970	Hydrogen	H ₂	1100 Å	A	Carruthers
1970	Hydrogen cyanide	HCN	3.4 mm	E	Snyder and Buhl
1970	Xogen	(HCO)+	3.4 mm	E	Buhl & Snyder
1970	Cyanoacetylene	C ₂ HCN	3.3 cm	E	Turner
1970	Methyl alcohol	CH ₃ OH	36.1 cm, 3 mm	E	Ball, Gottlieb, Lilley and Radford
1970	Formic acid	HCOOH	18 cm	E	Zuckerman, Ball and Gottlieb
1971	Carbon monosulfide	CS	2.0 mm	E	Penzias, Solomon, Wilson and Jefferts
1971	Silicon monoxide	SiO	2.3 mm	E	Wilson, Penzias, Jefferts, Kutner and Thaddeus

TABLE 1 (continued)

Year	Name	Symbol	Wavelength	Spectrum	Discoverer
1971	Methyl acetylene	C_2HCH_3	3.5 mm	E	Snyder & Buhl
1971	Isocyanic acid	HNCO	3.4 mm, 1.4 cm	E	Snyder & Buhl
1971	Carbonyl sulfide	COS	2.7 mm	E	Jefferts, Penzias, Wilson and Solomon
1971	Methyl cyanide	CH_3CN	2.7 mm	E	Solomon, Jefferts, Penzias and Wilson
1971	(Hydrogen isocyanide)	HNC	3.3 mm	E	Snyder & Buhl
1971	Formamide	NH_2CHO	3.3 mm	E	Rubin, Swenson, Benson, Tigelaar and Flygare
1971	Acetaldehyde	CH_3CHO	28 cm	E	Ball, Gottlieb, Lilley and Radford
1971	Thioformaldehyde	HCHS	9.5 cm	A	Sinclair, Ribes, Fourikis, Brown and Godfrey
1972	Formaldimine	HCHNH	5.7 cm	E	Godfrey, Brown, Robinson and Sinclair

So far, we know little more about most of the interstellar molecules than that their lines are present in the spectrum of this or that radio source. The direction from the center of the Milky Way has proved to be particularly rewarding. The radiolines are often very weak, so that it is difficult and tedious to observe many radio sources and to investigate them in detail. Some radio-molecules, though, are quite well known. In part, they have led to new and surprising insights, and have proved to be a valuable means to study the preliminary stages of stellar development on one hand, and dense and cool interstellar clouds on the other hand.

The Properties of the Molecular Sources

1. The Interstellar Masers (OH and H₂O)

The properties and particulars of the OH sources have been studied most productively so far. This is understandable because the hydroxyl radiation is the most intensive and the longest-known. We must distinguish between two types of OH sources. These are the area sources, which are detected essentially by absorption, and the point sources, which are characterized by unusually strong emission. The emission is so strong and singular that there was originally doubt about the correct identification, and some wished to consider a special material, "Mysterium", to be responsible for it. We shall now consider these mysterium sources in more detail.

Because of Λ -doubling and interaction with the spin of the hydrogen nucleus, the ground state of the hydroxyl molecule is split into four states. The four possible transitions between them give a line quartet at about 18 cm wavelength (see Figure 2).

The emission lines consist of many extremely narrow components. These are much narrower than we would expect, because of the mean turbulent motion in the interstellar clouds (Figure 3). Furthermore, the radiation is polarized, and variable over some weeks. The intensity is very high. If we wished to explain it by means of a hot gas, the gas would have to have a temperature of more than 10^9 K. The intensity ratios among the four lines are variable from source to source, and deviate very greatly from the equilibrium values. All these findings exclude consideration of thermal radiation with respect to the observed OH radiation.

The situation is quite similar for the H_2O sources. They also always show OH emission; but not all OH sources are also H_2O sources.

Depending on which of the four OH lines is the strongest, the OH sources can be divided into 3 classes, which are linked with different types of celestial bodies.

- I. Sources which radiate predominantly in the 1665 MHz line and rarely in the 1667 MHz line. They always occur in the vicinity of large HII areas (these are interstellar clouds in which the hydrogen is almost completely ionized by the ultraviolet radiation of nearby O stars).

Comparison of the radial velocities shows that this adjacency is not accidental. The OH source in the Orion nebula belongs in this class.

- IIa. The 1720 MHz line is strongest, and the other lines appear in absorption. Such sources are in the vicinity of the remnants of supernovas. Cassiopeia A is one example.

- IIb. The 1612 MHz line predominates, and the other lines are very weak. The origin of such hydroxyl radiation is the neighborhood of certain stars with strong infrared excess, such as VY Canis Majoris.

All OH sources are of very small extent (a few arc-seconds diameter). Interferometric observations with transcontinental baselines showed that these sources consist of single radiating points with diameters of 0.001" to 0.05". Each of these points provides one of the narrow components of the line profile. The more distant the sources, the greater is the angular diameter. Thus, we have not determined the true diameter. Instead, the radiation on its way to us is scattered by the inhomogeneities

in the distribution of the free electrons in interstellar space. Thus, radiating points become vague spots.

In order to explain the observed intensity of the radiation, we must assume a great amplification within the source. It is believed that this happens in the same manner as in the molecular amplifiers (masers and lasers). For the amplification effect it /133 is necessary that more molecules occur in the upper of two states linked by a transition than would be the case at equilibrium. Now if a wave with a length matching the transition strikes an excited molecule, this molecule gives up its energy to the wave and goes to its lower state. It is obvious that the radiation can be amplified considerably in this way, as long as enough excited molecules are present

In any case, it is not clear how enough molecules get into the proper states (this process is called pumping). In each case, different pumping processes must occur in the three classes of OH sources. For Class IIb, the first vibrational state appears to be excited by absorption of stellar infrared radiation with a wavelength of $2.8\ \mu\text{m}$. The desired transition occurs in the reversion to the ground state. The behavior is similar for Class IIa, but here the pumping is done by radiation with a wavelength of $120\ \mu\text{m}$, which places the molecules in the first excited rotational state.

Several pump mechanisms are being discussed to explain the Class I OH sources. There is some probability for the suggestion that water molecules are broken into OH and H by collisions with hydrogen atoms. The calculations show that the resulting OH molecules will be preferentially in the upper A-states, so that there will be a transition. This concept is supported by the fact that all H₂O sources are very strong OH radiators. Although not all hydroxyl sources also transmit water lines, this may be

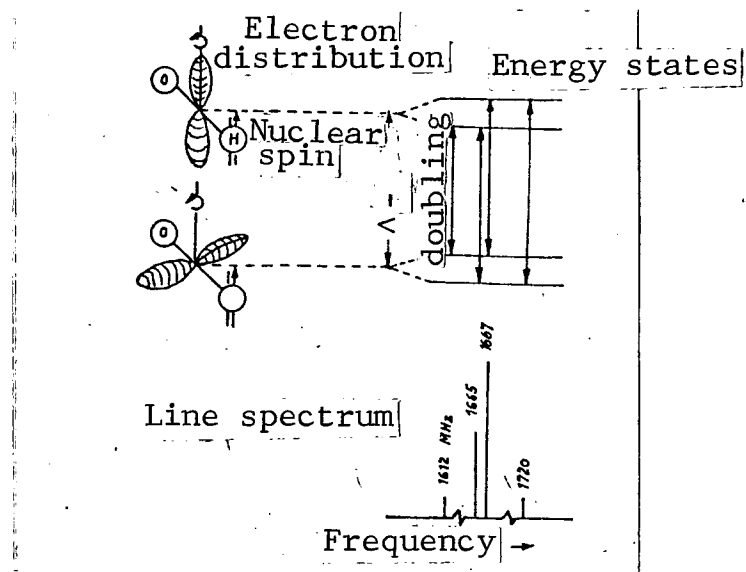


Figure 2: Schematic representation of the splitting of the hydroxyl radical rotational state and of the resulting spectrum.

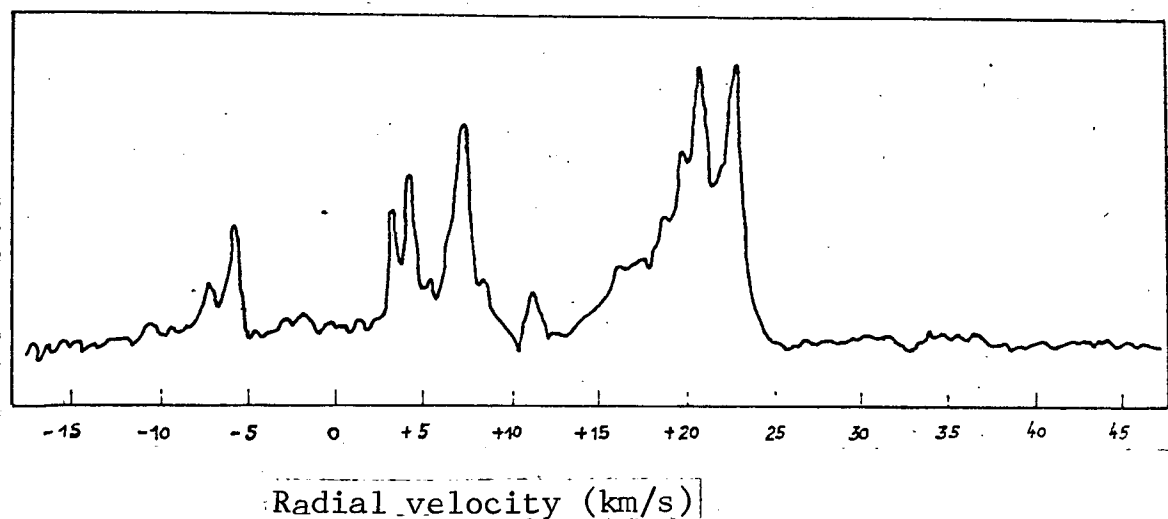


Figure 3: The profile of the 1665 MHz line in the direction of the Orion nebula. Note the many narrow components which make up the emission line.

because the H₂O masers require more limiting conditions.

The densities in the Class I OH sources are between 10^6 and 10^{14} hydrogen atoms per cm³. The lower limit ensures that the ultraviolet radiation which is able to dissociate the OH molecules is effectively shielded. At excessively high densities, a marked pressure broadening of the spectral lines would occur; it is not observed. In order to explain the radiation received, the individual radiating points must have dimensions on the order of 2×10^{14} cm. This value is in the range of those established for protostars. The energy radiated out is only a little below the light power of the sun. We cannot rule out the possibility, then, that in the hydroxyl sources we are seeing interstellar clouds on their way to becoming stars.

2. Formaldehyde

The 4.8 GHz line was observed in absorption in the direction of some dark clouds, although no marked increase in the continuous radio radiation could be measured (Figure 4). The formaldehyde molecules, then, absorb primordial radiation. Consequently, they must have a lower excitation temperature than about 3 K. In one case, even 0.8 K was found. This is the lowest temperature yet measured in interstellar space.

This finding is quite surprising, because the primordial radiation fills the entire universe, and the molecules should show at least its temperature. The lower excitation of the HCHO molecules indicates that the lower state is overpopulated. That is to say, we must seek for a process which will cool the formaldehyde below the ambient temperature.

We shall explain one possibility by means of Figure 5, which shows the possible states in the vicinity of the ground

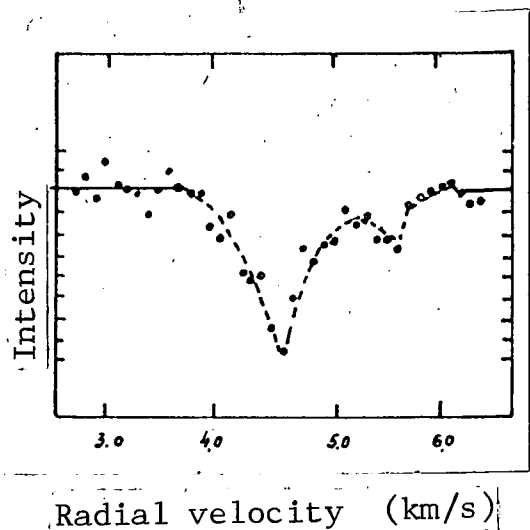


Figure 4: Absorption spectrum of formaldehyde at 4.8 GHz in the direction of a dark galactic cloud.

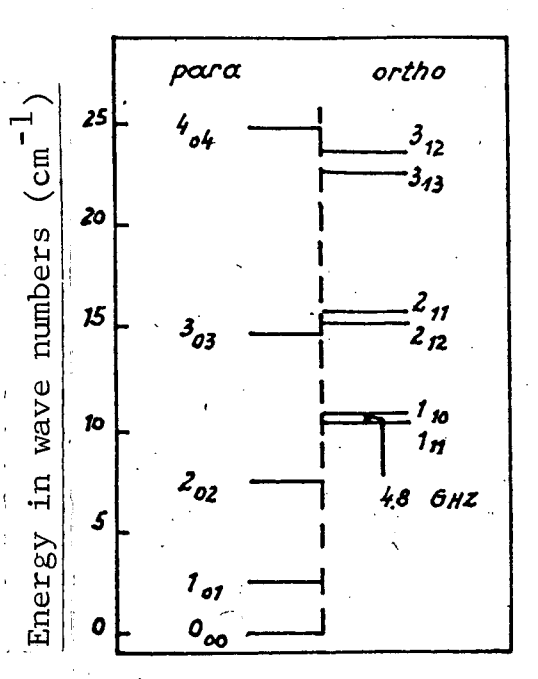


Figure 5: Schematic representation of the lowest rotational states of formaldehyde.

state by means of a schematic diagram. We shall not go into detail about the designations, and mention only that transitions from the left-hand ladder of states (so-called para-formaldehyde) to the right-hand one (ortho-formaldehyde) are very rare. Due to conservation of momentum and energy, the lower states of the pairs are preferentially excited by collisions from the states 1_{10} and 1_{11} . For instance, the transition $1_{10} \rightarrow 3_{13}$ occurs more frequently than the transition $1_{10} \rightarrow 3_{12}$. When energy is radiated away, the molecules then return to lower states. But in all cases, only transitions between the lower of the double states are allowed. Thus, for instance, $3_{13} \rightarrow 2_{12}$ is allowed, but not $3_{13} \rightarrow 2_{11}$. It is easy to see that this produces a collection of HCHO molecules in the 1_{11} state, from which the 4.8 GHz radiation is then absorbed.

Thus, our cooling machine works as follows: It takes kinetic energy from the gas and uses it to lower the temperature of the formaldehyde molecules.

3. Abundance of the Interstellar Molecules

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We have selected two particularly gross examples to show how far the conditions in interstellar space can diverge from thermodynamic equilibrium. The absence of equilibrium makes a conceptual explanation of the observations difficult, and our knowledge of the physical conditions in the molecular clouds is correspondingly incomplete.

The abundances of the various molecules in the direction of the center of the Milky Way and in the direction of Orion are listed in Table 2. The table shows numbers along the lines of sight (molecules per cm^2), which are directly derived from the observations alone. The exact density values depend on the extent of the clouds along the line of sight, which is unknown.

We could take approximately $1 \approx 10^{19} \text{ cm}^{-3}$ (≈ 3 light years) as an average value. Isotopic forms of many molecules have also been discovered. For example, lines of ^{18}OH , $^{13}\text{C}^{16}\text{O}$, $\text{H}^{13}\text{C}^{14}\text{N}$, and $\text{H}_2^{13}\text{C}^{16}\text{O}$ have been observed. Isotopic ratios have so far been determined only quite inaccurately. Therefore it is not yet possible to decide whether or not they differ from the terrestrial values.

TABLE 2. ABUNDANCE OF THE INTERSTELLAR MOLECULES

Molecule	Sagittarius	Orion
H_2	$\geq 10^{22} \text{ cm}^{-2}$	$\sim 2 \times 10^{23} \text{ cm}^{-2}$
OH	$> 5 \times 10^{16}$?
CO	$\sim 10^{19}$	$\sim 10^{18}$
CN	—	$\sim 10^{15}$
CS	$\sim 10^{14}$	$2 \times 10^{13} - 5 \times 10^{14}$
SiO	$\sim 4 \times 10^{13}$	—
HCN	?	$\sim 10^{15}$
COS	$\geq 3 \times 10^{15}$	—
NH_3	$\geq 10^{17}$	—
HCHO	$\sim 2 \times 10^{15}$	$\sim 3 \times 10^{14}$
C_2HCN	$\sim 2 \times 10^{16}$	—
HCOOH	$10^{13} - 3 \times 10^{15}$	—
CH_3OH	?	$\sim 5 \times 10^{16}$
CH_3CN	$\sim 2 \times 10^{14}$	—
Xogen	—	$\sim 10^{15}$

Formation and Destruction of the Molecules

Many formative and degrading processes are conceivable in interstellar space. A satisfactory explanation of the observed molecular abundances must decide which of these actually occur.

Ionization and dissociation through absorption of ultraviolet stellar radiation are the major causes for the destruction of interstellar molecules. Only CO, SiO, and CS have a lifetime of some 1,000 years under the average conditions. Thus, interstellar molecules probably occur only in rather dense clouds which are also rich in interstellar dust particles, because this is the only way in which the destructive starlight can be shielded effectively.

The interstellar molecular clouds are rather cool. The temperature is about 10 K. The molecules are excited to radiate by collisions with other gas particles, so that the clouds give off energy steadily, and their temperature sinks. In such a cool environment, the molecules freeze fast to the dust particles. That is, they stick to their surfaces if they collide with them. In this way, the molecules could gradually disappear from the gas.

Molecules can form, basically, from collision of the appropriate atoms. But the probability is very small for most of the compounds considered here, as the energy states of the atoms and of the molecules to be formed from them match very poorly. CH, CH⁺, CN and CO could originate in the observed amounts in this way.

The atmospheres of certain cool stars has been considered responsible not only for the production of interstellar dust particles, but also of the interstellar molecules. The low

resistance to stellar radiation makes this type of origin seem questionable, though. The surfaces of the interstellar dust particles are a very suitable place for the formation of molecules. They are very uneven, and have sharp edges and angles where impacting gas atoms could stick for a long time; long enough, for instance, to collide with a second one in the vicinity, with which they could combine. The liberated heat of formation disperses the dust particles, and the molecules return to the gas.

We can also conceive that fast particles (such as the cosmic rays) knock large particles off the dust surface, so that polyatomic compounds get into the gas. The dust particles could even be destroyed by heating, i.e. if a hot star begins to radiate in the neighborhood, having originated from the inner particles of the cloud itself. (A similar process goes on if a comet arrives in the vicinity of the sun. The dust particles and frozen gases of the comet head are vaporized, and the liberated gases form the tail).